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Random comb polymers,
process for preparing them and their use

Description

The present invention relates to random comb polymers
which have been prepared by free-radical polymerization
by the "catalytical chain transfer" process and also to
their use as dispersants for aqueous suspensions of
solids. They are suitable as additives for hydraulic
binders, in particular cement, but also lime, plaster
of Paris and anhydrite. The use of these copolymers
leads to a significant improvement in the building
materials produced therefrom during processing and
curing.

Additives are often added in the form of dispersants to
aqueous suspensions of pulverulent inorganic or organic
substances, e.g. hydraulic binders (cement, lime,
plaster of Paris or anhydrite), ground rock, ground
silicate, chalk, clays, porcelain slips, talc,
pigments, carbon black or polymer powders, ·in order to
improve their processability, e.g. kneadability,
flowability, sprayability, paintability or pumpability.
These additives are able to break up agglomerates by
adsorption onto the surfaces of the particles and to
disperse the particles formed. This leads, particularly
in the case of highly concentrated dispersions, to a
significant improvement in the processability.

In the production of building material mixtures
containing hydraulic binders such as cement, lime,
plaster of Paris or anhydrite, this effect can be
utilized particularly advantageously, since otherwise
significantly more water would be required to achieve a
processable consistency than would be necessary for the
subsequent hydration or curing process. The water which
gradually evaporates after curing leaves voids which
significantly impair the mechanical strength and

stability of the building components.

To reduce the proportion of water which is excess to hydration requirements and/or to optimize the
5   processability at a given water/binder ratio, additives which are generally referred to as water reduction agents or fluidizers and also as superplasticizers are used.

10 The still most frequently used fluidizers are polycondensation products based on naphthalenesulfonic or alkylnaphthalenesulfonic acids (cf. EP-A 214 412) and also melamine-formaldehyde resins containing sulfonic acid groups (cf. DE-C 16 71 017).
15

However, these fluidizers have the disadvantage that their good fluidizing action, in particular in concrete construction, is retained for only a relatively short time even at relatively high added amounts. This
20 decrease in the flowability of concrete mixtures is also referred to as "slump loss". It leads to problems particularly when relatively long periods of time elapse between production of the concrete and its installation, as often result from long transport or
25 conveying distances.

Furthermore, the liberation of toxic formaldehyde, which is present as a result of the production process, can lead to significant occupational hygiene hazards if
30 processing is carried out in the interior of a building (production of prefabricated concrete components or drying of gypsum plasterboard) or in mining or tunnel construction.

35 To circumvent these disadvantages, formaldehyde-free fluidizers based on maleic monoesters and styrene have been developed (cf. EP-A 306 449). Although these additives enable a high dispersion performance to be

achieved over a sufficient period of time (low slump loss), these positive properties are quickly lost on storing the aqueous preparations of these fluidizers. The low storage stability of these fluidizer solutions can be attributed to the ease with which the maleic monoesters hydrolyze.

To circumvent this problem, various hydrolysis-stable fluidizers have been developed. All these fluidizers are copolymers of ethylenically unsaturated carboxylic acids (e.g. acrylic acid, methacrylic acid or maleic acid or their salts) and poly(alkylene oxides) having a polymerizable end group (e.g. methacrylates, allyl ethers or vinyl ethers). The incorporation of these long-chain monomers into a polymer chain leads to polymers having a comb-like structure (cf. US 5,707,445 B1, EP 1 110 981 A2, EP 1 142 847 A2).

These comb polymers have a high storage stability together with a significantly improved effectiveness compared to fluidizers based on lignin, naphthalene or melamine condensate.

According to a widely accepted theory, the effectiveness of the fluidizers is based on two different effects. Firstly, the negatively charged acid groups of the fluidizers adsorb on the cement particle surface which is positively charged due to calcium ions. The resulting electrostatic double layer (zeta potential) leads to electrostatic repulsion between the particles. However, the repulsion forces caused by the zeta potentials have only a short range (cf. H. Uchikawa, Cement and Concrete Research 27 [1] 37-50 (1997)).

However, the physical presence of the adsorbed fluidizer also prevents the surfaces of the cement particles from coming into direct contact with one

another. This steric repulsion effect is greatly
increased by the nonadsorbed side chains of the
abovementioned comb polymers (cf. K. Yoshioka, J. Am.
Ceram. Soc. 80 [10] 2667-71 (1997)). It is self-evident
that the steric repulsion effect can be influenced both
by the length of the side chains and by the number of
side chains per main chain. On the other hand, a side
chain density or length which is too high can hinder
the adsorption on the cement particle surface. To
determine the degree of adsorption of a fluidizer on
cement particles, the content of organic material is
determined (TOC analysis) after addition of the
fluidizer to the make-up water. After the cement has
been stirred in and the mixture has been left for a
short time, the water is pressed out of the cement
binder and the collected pore water is analyzed once
again by means of TOC analysis. The decrease in the TOC
value then corresponds to the proportion of adsorbed
fluidizer. It has been able to be shown by means of
such measurements that large parts of the fluidizer are
not adsorbed. This is not surprising since the side
chains are not stretched out in solution but are
presumably present in tangled form. As a result,
carboxylate groups in the immediate vicinity of the
side chain are sterically shielded from the cement
particle and cannot contribute to adsorption.

In addition, the preparation of the fluidizers by free-
radical copolymerization of a plurality of different
monomers leads to relatively nonuniform products in
respect of molecular weight and side chain density. It
is therefore not surprising that part of these
fluidizers is not adsorbed on the cement particle
surface but remains dissolved in the pore water. If the
main chain is too short or the side chain density is
too high, it is possible, for example, for the number
of carboxyl groups accessible to the cement particle
surface to be insufficient. On the other hand, main

chains which are too long and have a low side chain
density can bridge cement particles and thus promote
flocculation. These nonadsorbed amounts presumably make
no contribution to the water reduction capability of
5   the fluidizer.

As mentioned above, the polymeric fluidizers known from
the prior art for cement-containing systems are
copolymers which have a comb-like structure and are
10   prepared by means of free-radical polymerization. All
these products have a high degree of nonuniformity in
respect of the number of side chains per polymer
molecule and in respect of the molecular weight.
However, it is known that there is an optimum molecular
15   weight and an optimum number of side chains per polymer
molecule for each application and each type of cement.
All constituents of a product which deviate from this
optimum therefore reduce the effectiveness of the
product or make higher added amounts necessary.
20   Furthermore, it is known that polymers having an
excessively high molecular weight can have a
coagulating action.

According to the German patent application
25   102 37 286.1, it has been found that linear
polyethylene oxide-polycarboxylic acid block copolymers
having low molecular weights in the range from 1000 to
20 000 g/mol surprisingly have a better fluidizing
action than commercial products based on comb-like
30   polyether carboxylates.

However, the synthesis of the block polymers described
in the patent application DE 102 37 286.1 by means of
atom transfer radical polymerization (ATRP) is
35   relatively complicated. Since free (meth)acrylic acid
cannot be polymerized directly in a controlled fashion
by means of ATRP, a circuitous route via the
corresponding tert-butyl ester of (meth)acrylic acid

has to be employed. Owing to the fact that these esters
and largely insoluble in water, the ATRP has to be
carried out either in bulk or in organic solvents. The
polymerization is then followed by the acid-catalyzed,
selective cleavage of the tert-butyl ester groups,
resulting in liberation of isobutylene. Furthermore,
the ATRP catalysts have a relatively strong corrosive
effect on steel reactors. ATRP is thus not optimal for
industrial production.

It is therefore an object of the present invention to
provide polymer compounds which have a similarly good
effectiveness as the above-described linear block
copolymers but are substantially simpler to synthesize.

This object is achieved by the provision of random comb
polymers which have been prepared by free-radical
copolymerization of a vinylic poly(alkylene oxide)
compound (A) with at least one ethylenically
unsaturated monomer compound (B) by the "catalytical
chain transfer" polymerization method (CCT).

CCT polymerization is described in more detail in the
following patents and publications: US 4,526,945 B1,
US 4,680,354 B1,   EP   196 783 A1,   EP 199 436 A1,
WO 87/03 605 A1, DE 694 23 653 T2, N.S. Enikolopyan et
al., J. Polym. Sci., Polym. Chem. Ed., (1981), 19, 879;
D.M. Haddleton et al., Journal of Polymer Science, Part
A: Polymer Chemistry (2001), 39(14), 2378-2384.

CCT makes it possible to prepare polymers or oligomers
having significantly lower molecular weights than is
possible via conventional free-radical polymerization.

While it is very difficult to obtain molecular weights
below 6000 g/mol by means of conventional free-radical
polymerization, even when using equimolar amounts of
thioregulators, based on the monomers, CCT makes it

possible to produce polymers having very low molecular weights (less than 50 000 g/mol, in particular less than 4000 g/mol) without difficulties. The amount of CCT catalyst required is a number of orders of magnitude lower than in the case of conventional (thio)regulators. This leads not only to a significant reduction in production costs, but also helps to avoid the odor pollution which is unavoidable when using large amounts of thioregulators.

These novel random comb polymers prepared by means of CCT polymerization surprisingly display a better water reduction capability at the same added amount than conventional fluidizers based on comb polymers. Furthermore, the concrete after addition of these novel fluidizers displays a signficantly reduced stickiness and plastic viscosity, which greatly improves, in particular, the processability of very cement-rich concretes. The company NMB Ltd. has coined the term "rheosmooth" to describe this particular processing property of the concrete. It is also noteworthy that concretes which have been produced using the fluidizers of the invention display a significantly greater spread compared to those produced using conventional polycarboxylate ether fluidizers at the same slump. Thus, at the same water/cement ratio, the concretes display a greater shear-thinning behavior than conventional concretes, but without displaying a tendency to segregate ("bleed").

In addition, the slump loss can be reduced compared to conventional fluidizers by varying the monomer ratios, which was likewise not foreseeable.

The random comb polymers of the invention are obtainable by free-radical copolymerization of a vinylic poly(alkylene oxide) compound (A) with an ethylenically unsaturated monomer compound (B) in the

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presence of CCT catalaysts.

The vinylic poly(alkylene oxide) compound (A) used according to the invention corresponds to the general formula (I)

$$R^1\!\!-\!\!O\!\!-\!\!(\!C_mH_{2m}O\!)_{\overline{n-1}}\!C_mH_{2m}\!\!-\!\!Z \qquad (I)$$

where R^1 has the following meaning: a hydrogen atom, an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, a cycloaliphatic radical having from 5 to 12 carbon atoms or an aryl radical having from 6 to 14 carbon atoms, which may optionally be substituted. Suitable substituents are, for example, hydroxyl, carboxyl or sulfonic acid groups. The indices have the following meanings: $m = 2$ to 4 and $n = 1$ to 250, with m preferably being 2 or 3 and n preferably being 5 to 250 and more preferably from 20 to 135.

Preferred cycloalkyl radicals are cyclopentyl or cyclohexyl radicals, and preferred aryl radicals are phenyl or naphthyl radicals which, in particular, may be substituted by hydroxyl, carboxyl or sulfonic acid groups.

For the purposes of the present invention, the building block Z has the following meanings: Z is derived from vinylically unsaturated compounds of the general formula

$$\begin{array}{c} \mathrm{O} \\ \parallel \\ \mathrm{Y\!-\!C\!-\!C\!=\!C_{m'}H_{2m'}} \\ | \\ \mathrm{C_{n'}H_{2n'+1}} \end{array}$$
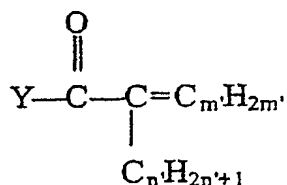
Here, m' can be from 1 to 4 and n' can be 0, 1 or 2, with preference being given to m' = 1 and n' = 0 or 1. Y can be O or NR^2, and R^2 can be H, an alkyl radical having from 1 to 12 carbon atoms or an aryl radical having from 6 to 14 carbon atoms or $-C_mH_{2m}(O-C_mH_{2m})_{n-1}OR^1$, where R^1, m and n are as defined above. Particular preference is given to R^2=H, CH_3 or C_2H_5.

Comonomers used are (free radically) polymerizable ethylenically unsaturated monomer compounds (B) of the general formula (II). For the preparation of dispersants, water-soluble ethylenic unsaturated compounds are particularly suitable.
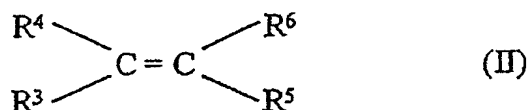
$$R^4 \diagdown \quad \diagup R^6$$
$$\qquad C = C \qquad \qquad (II)$$
$$R^3 \diagup \quad \diagdown R^5$$

R^4 can be H or a substituted or unsubstituted C_6-C_{14}-aryl radical. Suitable substituents are, for example, hydroxyl, carboxyl or sulfonic acid groups. R^3 and R^5 can be H, CH_3, COOH or their salts, $COOR^7$, $CONR^7R^7$ or $-C_mH_{2m}(O-C_mH_{2m})_{n-1}OR^1$, where preference is given to using alkali metal (sodium, potassium), alkaline earth metal (calcium) or ammonium salts as carboxylic acid salts and R^1, m and n are as defined above.

R^7 can be H, C_1-C_{12}-alkyl, C_1-C_{12}-hydroxyalkyl, C_1-C_{12}-alkylphosphate or -phosphonate and salts thereof (alkali metal, alkaline earth metal or ammonium salts) or C_1-C_{12}-alkylsulfate or -sulfonate and salts thereof (alkali metal, alkaline earth metal or ammonium salts).

R^3 and R^5 in the formula (I) can together form an -O-CO-O- group, so that the corresponding monomers are derived from maleic anhydride. R^5 can also be a

substituted or unsubstituted C_6-C_{14}-aryl radical or OR^8, where R^8 = acetyl. Suitable substituents are, for example, hydroxyl, carboxyl or sulfonic acid groups.

5   Finally, R^5 can also be PO_3H_2, SO_3H or $CONH$-R^9 or an alkali metal, alkaline earth metal or ammonium salt thereof. R^9 is in this case C_1-C_{12}-alkylphosphate or -phosphonate or a salt thereof, C_1-C_{12}-alkylsulfate or -sulfonate or a salt thereof, with the alkali metal,

10 alkaline earth metal and ammonium salts being possible as salts in each case. R^6 is H, CH_3 or CH_2-$COOR^7$, where R^7 is as defined above.

To prepare the copolymers of the invention, preference

15 is given to using monomer compounds in which R^3 and R^4 = H or R^3 and R^5 together form an O-CO-O group, R^6 = H, CH_3 or CH_2-$COOR^7$ and R^5 = $COOR^7$, PO_3H_2, SO_3H or $CONH$-R^9-SO_3H or a phenyl radical which may optionally be substituted by hydroxyl, carboxyl or sulfonic acid groups.

20 Preference is given to R^3 and R^4 = H, R^6 = H, CH_3 and R^5 = $COOR^7$, PO_3H_2 or $CONH$-R^9-SO_3H and very particularly preferably R^3 and R^4 = H, R^6 = CH_3, R^5 = COOH or a salt thereof or $COOR^7$ and R^7 = C_1-C_6-hydroxyalkyl.

25 The comb polymers of the invention can have molar ratios of vinylic poly(alkylene oxide) compound (A) to ethylenically unsaturated monomer compound (B) of from 1:0.01 to 1:100. However, preference is given to ratios of from 1:0.1 to 1:50 and particular preference is

30 given to ratios of from 1:1 to 1:35.

According to the invention, the comb polymers are prepared by free-radical polymerization in the presence of CCT catalysts and suitable initiators at

35 temperatures of from 30 to 150°C.

In a preferred embodiment, the polymerization is carried out in the presence of CCT catalysts as are

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described in EP 739 359 B1. These catalysts preferably have the following general formula (III),

(III)
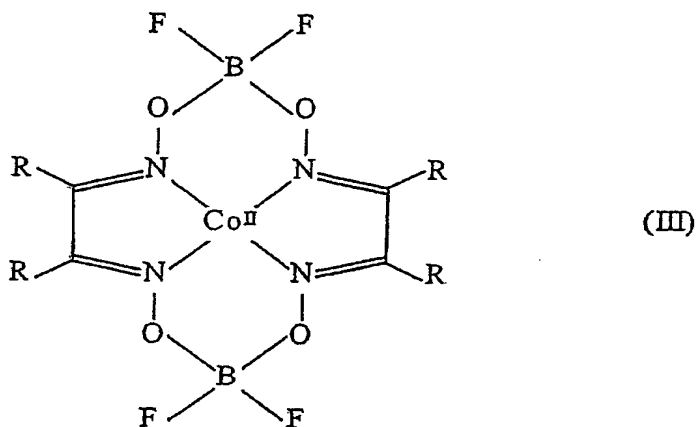
5

where R is, in particular, a methyl group.

To carry out the polymerization under CCT conditions,
the monomers and solvents, preferably water, are
10 firstly freed of oxygen by methods known to those
skilled in the art of polymerization or organic
synthesis. This can be achieved, for example, by
passing nitrogen, argon or another nonoxidizing gas
through the solution. The monomer solution is then
15 admixed with an initiator (in particular an azo
initiator or redox system) and the CCT catalyst and is
heated. Suitable azo initiators should be soluble in
the reaction mixture and have a half-life appropriate
to the reaction temperature.

20

Without making any claim to completeness, the following
azo initiators are particularly suitable for
polymerizations in an aqueous medium: 2,2'-azobis[2-
methylpropionamidine) dihydrochloride (CAS 2997-92-4),
25 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydro-
chloride (CAS 27776-21-2) or 4,4''azobis[4-cyano-
pentanoic acid] (CAS 2638-94-0). The polymerization
temperature depends on the thermal half-life of the azo

initiator used. The reaction temperatures are usually in the range from 30 to 150°C, preferably from 40 to 100°C and more preferably from 50 to 80°C.

5   In a modification of the above-described method, it is also possible to meter in one or more monomer components during the reaction. Furthermore, part of the CCT catalyst can be charged initially and part can be metered in during the course of the polymerization.

10   It is also possible to meter in the total amount of the catalyst during the course of the polymerization, but this usually leads to more nonuniform products.

Although a substantial freedom from oxygen is critical
15   to the success of CCT polymerizations, i.e. for the preparation of polymers having low molecular weights and monomodal molecular weight distributions, it has been found that it is surprisingly possible, nevertheless, to initiate CCT polymerizations by means
20   of redox systems. In this case, it is critical that the reducing component is initially charged and the oxidizing component is slowly metered in during the course of the polymerization. It is possible to use, inter alia, hydrogen peroxide, tert-butyl
25   hydroperoxide, benzoyl peroxide, lauroyl peroxide and persulfates as oxidation component. Suitable reducing agents are metal salts which can be converted into a higher oxidation state, for example iron(II) sulfate, ascorbic acid and hydroxymethanesulfinates and
30   derivatives and salts thereof.

The present invention further provides for the use of the comb polymers of the invention as dispersants for aqueous suspensions of solids, wherein the respective
35   comb polymers are used in an amount of from 0.01 to 5% by weight, based on the respective suspension of solids.

It is possible within the scope of the present invention for the respective suspension of solids to comprise inorganic particles which are selected from the group consisting of ground rock, ground silicate,

5   chalk, clays, porcelain slips, talc, pigments and carbon black.

The comb polymers of the invention are particularly preferably used for hydraulic binder suspensions based

10   on cement, lime, plaster of Paris and anhydrite. The comb polymers of the invention here display a better water reduction capability at the same added amount compared to conventional fluidizers based on comb polymers corresponding to the prior art.

15

In addition, the corresponding building material mixtures after addition of these comb polymers display considerably reduced stickiness and plastic viscosity, which greatly improves, in particular, the

20   processability of very cement-rich building material mixtures, e.g. concretes. In addition, the building material mixtures using the fluidizers proposed according to the invention display a signficantly higher spread at the same slump compared to mixtures

25   comprising conventional polycarboxylate ether fluidizers. The building material mixtures and in particular concretes thus have a stronger shear-thinning behavior than conventional concretes at the same water/cement ratio, but without tending to

30   segregate ("bleed").

Random comb polymers which are obtainable by free-radical copolymerization of a vinylic poly(alkylene oxide) compound (A) with an ethylenically unsaturated

35   monomer compound (B) by the "catalytical chain transfer (CCT)" method are described. These comb polymers are highly suitable for hydraulic binder suspensions based on cement, lime, plaster of Paris and anhydrite, since

they display a better water reduction capability at the same added amount than the conventional fluidizers based on comb polymers based on the prior art. In addition, the corresponding building material mixtures after addition of these comb polymers have a significantly reduced stickiness and plastic viscosity, which, in particular, greatly improves the processability of very cement-rich building material mixtures such as concretes. Furthermore, the building material mixtures using the fluidizers proposed according to the invention display a significantly higher spread at the same slump compared to mixtures comprising conventional polycarboxylate ether fluidizers. The building material mixtures and in particular concretes thus have a stronger shear-thinning behavior at the same water/cement ratio than conventional concretes, but without tending to segregate ("bleed").

The following examples and the accompanying drawing illustrate the invention.

Fig. 1 GPC chromatogram for Example A.6. RI detection
         Mobile phase: mixture of 80% of 0.05 M aqueous
         ammonium formate solution and 20% of
         acetonitrile; column combination (from Showa
         Denko): Shodex OHpak SB-804 HQ (8 mm × 300 mm)
         and Shodex OHpak 802.5 HQ (8 mm × 300 mm) and a
         Shodex OHpak SB-G (6 mm × 50 mm) as precolumn.
         Column packing: polyhydroxymethyl methacrylate.

Examples

A.   General methods for the synthesis of the
     fluidizers according to the invention by means of
     CCT

Variant 1

A 500 ml three-necked flask is provided with precision
glass stirrer, an inlet for inert gas (nitrogen), gas
wash bottle for discharge of inert gas, a metering pump
for metered addition of monomer solutions and a heating
5   bath. Furthermore, a stock vessel for the monomer
solution is required, and this likewise has to be made
oxygen-free by means of inert gas.

20 ml of water and the azo initiator are placed in the
10   flask. The solution is subsequently made oxygen-free by
passing the inert gas through it.

The monomers are placed in the stock vessel as a
mixture and are, if necessary, diluted with water so
15   that a pumpable solution is obtained. The monomer
solution in the stock vessel is likewise made oxygen-
free by paaring inert gas through it.

The cobalt complex is then introduced into the reaction
20   vessel, inert gas is once again passed through for
10 minutes and the reaction vessel is finally heated to
a temperature at which the azo initiator used has an
appropriate half-life (about 45 to 90 min). The monomer
mixture is fed in from the stock vessel over the entire
25   reaction time. In the case of the examples described
below, the monomer is metered in linearly.

The reaction is complete when no appreciable amounts of
monomer can be detected by means of GPC or GC. This is
30   generally the case after from 4 to 8 hours. Variant 1
can be used advantageously when all monomers used have
similar polymerization rates. This is the case, for
example, when using short-chain polyethylene glycol
monomethyl ether methacrylates (MPEG-MA) for the
35   synthesis of the copolymers according to the invention.

Variant 2
A 500 ml three-necked flask is provided with precision

glass stirrer, an inlet for inert gas (nitrogen), gas wash bottle for discharge of inert gas, a metering pump for metered addition of monomer solutions and a heating bath. Furthermore, a stock vessel for the monomer 5 solution is required, and this likewise has to made oxygen-free by means of inert gas.

The macromonomer (MPEG-MA) and the azo initiator are placed in the flask and diluted with water so that a 10 readily stirrable solution is formed. The water content is usually 50% by weight. The solution is subsequently made oxygen-free by passing the inert gas through it.

The cobalt complex is then added, and inert gas is 15 passed through for another 10 minutes. The reaction temperatures and times are the same as in variant 1. The comonomer from the stock vessel is fed in over the entire reaction time. In the case of the examples described below, the monomer is metered in linearly.
20
Examples of the synthesis of copolymers according to the invention are summarized in Table 1. Here, MA is methacrylic acid, IT is itaconic acid, HEMA is hydroxyethyl methacrylate, EGMAP is ethylene glycol 25 monomethacrylate phosphate and V44[TM] is 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride. The mean molecular weight of the MPEG substituent of the MPEG-MA used is in each case shown in the 4th column.

Example No.	Variant	MA [mol]	IT [mol]	HEMA [mol]	EGMAP [mol]	MPEG-MA [mol]	V44™ [mg]	Cocat. [mg]	Temp. [°C]	Reaction time [h]	M_w [g/mol] PD
A.1	1	0.27	x	x	x	350 / 0.17	600	21	60	6	5790 / 1.5
A.2	1	0.65	x	x	x	350 / 0.22	1200	45	60	6	6100 / 1.52
A.3	1	0.27	x	x	x	475 / 0.17	600	22	60	5	6200 / 1.49
A.4	1	0.65	x	x	x	475 / 0.22	1200	44	60	6	5870 / 1.43
A.5	1	0.65	x	x	x	475 / 0.07	1200	43	60	8	6230 / 1.47
A.6	1	0.84	x	x	x	475 / 0.028	1200	64	60	8	6090 / 1.56
A.7	1	0.76	x	0.08	x	475 / 0.054	1200	43	60	3	6100 / 1.49
A.8	2	0.55	x	x	x	750 / 0.11	300	22	60	5	7950 / 1.55
A.9	2	0.8	x	x	x	750 / 0.08	600	45	60	4	7190 / 1.54
A.10	2	0.84	x	x	x	750 / 0.028	1200	64	60	6	6240 / 1.57
A.11	2	0.27	0.11	x	x	750 / 0.054	600	22	60	6	7000 / 1.51
A.12	2	0.54	x	0.27	x	750 / 0.054	600	25	60	6	9100 / 1.62
A.13	2	0.64	x	0.21	x	750 / 0.043	600	25	60	6	9000 / 1.58
A.14	2	0.067	x	x	0.057	750 / 0.084	300	53	60	6	10230 / 1.78
A.15	2	0.4	x	x	x	1100 / 0.07	600	25	60	5	7300 / 1.63
A.16	2	0.5	x	x	x	1100 / 0.05	600	21	60	6	7730 / 1.51
A.17	2	0.16	x	x	x	1100 / 0.05	300	11	60	6	12120 / 1.64
A.18	2	0.8	x	x	x	2000 / 0.04	600	22	60	5	9330 / 1.49
A.19	2	0.4	x	x	x	4500 / 0.013	600	22	60	7	12300 / 1.61
A.20	2	0.4	x	x	x	4500 / 0.008	600	25	60	7	10800 / 1.6

Table 1

Figure 1 shows the GPC chromatogram of Example A.6. The chromatograms of the remaining polymers according to the invention are very similar to this example. The polydispersities are usually below 1.6 and are therefore significantly lower than the polydispersities which can be achieved by means of conventional free-radical polymerization techniques.

B.   Mortar tests for determining the water reduction capability and retention of the flowability over a period of 90 minutes

The tests were carried out in accordance with DIN EN 1015-3.

Table 2: Results of the mortar spread tests using CEM I 42.5 R v.02.03 Karlstadt

Rilem mixer; cement: Karlstadt; S/C=2.2 Standard sand = 70%; silica sand = 30%				spread of mortar:				
Example	Fluidizer	W/C	Add. [%]	0min [cm]	30min [cm]	60min [cm]	90min [cm]	Δ [cm]
B.1	A.1	0.46	0.2	21.6	21.5	21.5	21	0.6
B.2	A.2	0.46	0.2	24.5	22.7	22.8	22.3	2.2
B.3	A.3	0.47	0.2	23	22	21.4	21.3	1.7
B.4	A.4	0.4	0.25	25.2	24	23	22.6	2.6
B.5	A.5	0.4	0.2	25.5	21.9	21.2	20.6	4.9
B.6	A.6	0.4	0.2	23.4	21.2	20.3	20.3	3.1
B.7	A.7	0.46	0.2	25.5	23.1	22.5	21.8	3.7
B.8	A.8	0.37	0.2	24.6	20.7	20.1	19.6	5.0
B.9	A.9	0.38	0.2	24.2	22.3	21.2	20.5	3.7
B.10	A.10	0.44	0.2	24.4	21.5	20.4	20	4.4
B.11	A.11	0.37	0.2	22.7	19.4	19.4	18.9	3.8
B.12	A.12	0.42	0.2	22.7	20.9	20.9	20.7	2.0
B.13	A.13	0.44	0.2	23.8	22.5	22.4	22.5	1.3
B.14	A.14	0.44	0.2	24	21.8	21.8	21.4	2.6
B.15	A.15	0.44	0.2	24.7	21.6	21.7	21.4	3.3
B.16	A.16	0.42	0.2	25.6	22.7	22.2	21.3	4.3
B.17	A.17	0.47	0.2	22.5	21.7	21.3	21.6	0.9
B.18	A.18	0.41	0.2	24	20.3	20.8	18.5	5.5
B.19	A.19	0.4	0.2	23	19.3	18	16.8	6.2
B.20	A.20	0.38	0.2	23.1	18.2	17.6	16.5	6.6
B.21	without additive	0.48	0	20.6	-	-	-	-
B.22	Glenium® 27	0.48	0.2	23.1	23	23	22.9	0.2
B.23	Glenium® 51	0.4	0.2	24.7	22.8	22.1	21.8	2.90

Table 2

The commercial products Glenium® 51 and Glenium® 27 were employed as reference substances. While in the case of Glenium® 51 (Example B.23) the system was optimized to achieve a maximum water reduction, in the case of Glenium® 27 (Example B.22), the maintenance of processability over a period of 90 minutes was the main objective. Example B.21 reflects the behavior of a mortar without additional fluidizers. At a W/C ratio of 0.48, an initial spread of about 20 cm is achieved. However, the mortar stiffens so quickly that no spread can be determined after only 10 minutes. When Glenium® 27 is added to a mortar having an identical W/C of 0.48, the spread increases only moderately to about 23 cm, but the consistency remains virtually unchanged for

a period of 90 minutes.

It can clearly be seen from Table 2 that all fluidizers according to the invention which were tested have a

5   strong fluidizing action. It is in all cases greater than the action of Glenium® 27.. As can be seen from Examples B.1, B.13 and B.17, the choice of a suitable monomer composition even makes it possible to achieve a consistency retention comparable to Glenium® 27 at a

10   lower W/C value.

It can be seen from Examples B.4, B.5, B.6, B.8, B.9, B.11 and B.20 that the water reduction capability of Glenium® 51 can also be surpassed by use of polymers

15   according to the invention.

It is also noteworthy that even at very high spreads of > 26 cm (not shown in Table 2), no segregration ("bleeding") occurs, as would be the case for

20   conventional fluidizers without addition of specific stabilizers.

C.   Concrete tests for determining the water reduction
      capability and retention of the flowability over a

25   period of 90 minutes

The tests were carried out in accordance with DIN EN 206-1, DIN EN 12350-2 and DIN EN 12350-5.

30   Cement: CEM I 42.5 R v.02.03 Karlstadt (285 kg), amount of fluidizer added: 0.02% based on solids; temperature: 20°C. The results are summarized in Table 3.

In this test series, the water/cement ratio was

35   selected so that a uniform slump value of about 20 cm was achieved for all samples after completion of mixing. Here too, Glenium® 51 and Glenium® 27 served as reference substances.

As in the mortar, the polymers according to the invention display a significant fluidizing action in concrete, too. If only the slump value is considered, it is conspicuous that this usually drops to a greater extent over a period of 90 minutes than is the case for the reference substances Glenium® 51 and 27. The slump value is a measure of the degree to which the concrete cake collapses after the metal cone is lifted off (height difference between the upper edge of the metal cone and the height of the concrete cake after the metal mold has been taken off). The slump flow corresponds to the base diameter of the concrete cone after the concrete has slumped.

Exa-mple	Fluid-izer	w/c	Slump in [cm]					Slump flow in [cm]					Spread in [cm]				
			0	10	40	60	90	0	10	40	60	90	0	10	40	60	90
C.1	A.1	0.6	18.5	17	13	14	9	34	28	25	25	21	55	55	52	52	49
C.2	A.2	0.6	20.5	20.5	19	15.5	15	36	36	32	28	27	61	61	57	55	53
C.3	A.4	0.6	19.5	20.5	19.5	20.5	18	39	39	37	34	33	63	65	62	59	55
C.4	A.5	0.59	19	19	16.5	15	14	34	34	29	27	25	59	58	55	53	51
C.5	A.7	0.60	21	22	19.5	19	17	36	38	31	30	28	62	62	59	57	55
C.6	A.8	0.60	19.5	19	17	7		31	30	26	20		62	60	55	54	
C.7	A.8	0.60	20.5	20	19	19	17	36	37	31	33	31	61	61	59	56	54
C.8	A.9	0.55	20.5	19.5	16.5	5.5		38	34	28	20		61	59	53	50	
C.9	A.9	0.6	20.5	20	19	18		32	31	27	27		61	60	58	57	
C.10	A.10	0.58	20.5	19	14	12.5	6.5	33	31	27	26	20	58	58	54	52	50
C.11	A.11	0.55	20.5	18.5	6			35	31	20			59	56	49		
C.12	A.12	0.58	20	18	17	6		30	28	28	20		60	57	55	50	
C.13	A.13	0.58	20.5	21	16.5	13		35	35	29	25		61	59	57	54	
C.14	A.14	0.59	18.5	18.5	17	16		28	28	25	24		58	57	56	53	
C.15	A.15	0.57	20.5	18	17	15.5	7.5	41	37	30	27	20	61	60	53	51	49
C.16	A.15	0.59	20.5	19.5	17.5	15	14.5	41	38	34	26	26	64	61	55	54	50
C.17	A.16	0.59	20.5	20.5	18	19	17	39	36	32	30	28	64	62	57	55	52
C.18	A.16	0.62	21	21	19	18	16.5	38	38	35	33	31	62	62	59	58	55
C.19	A.17	0.59	19.5	19.5	18	16	14	33	33	29	25	27	58	57	54	52	50
C.20	A.18	0.59	21.5	20.5	20.5	18.5	15	44	39	33	32	26	64	63	58	55	51
C.21	A.19	0.59	19.5	20	15.5	14	7	37	36	27	24	21	57	57	52	50	47
C.22	A.20	0.56	20	18	15.5	13.5	12	35	30	27	26	25	59	57	52	50	49
C.23	Gl.51	0.55	20	20	18.5	16.5	16.5	39	37	32	28	28	59	58	55	53	49
C.24	Gl.27	0.62	19.5	20.5	21	19.5	20.0	30	34	33	32	32	57	59	58	57	55

Table 3: Gl. 51 = Glenium® 51, Gl. 27 = Glenium® 27

The spread is obtained by shaking the spread table, as described in the abovementioned DIN methods, by lifting and bumping it down 10 times. The shear forces generated by the "knocking" cause further spreading of the concrete. The diameter of the concrete cake after "knocking" is referred to as the spread. If slump and spread are now compared for the reference substances

Glenium® 51 and 27 on the one hand and the polymers
according to the invention on the other hand, it is
conspicuous that the latter have, immediately after
mixing (0 min), a greater spread at a comparable slump
5   (Examples C.2, C.3, C.5, C.6, C.7, C.8, C.9, C.12,
C.13, C.15, C.16, C.17, C.18, C.20). The differences
are even more drastic when the slump values are
compared with the corresponding spread values after 60
and 90 minutes. After 90 minutes, Glenium® 51 displays
10 a slump of 16.5 cm and a spread of 49 cm. If Examples
C.1, C.6, C.8, C.10, C.11, C.12, C.15 and C.22 are
regarded for comparison, it becomes clear that a spread
of over 49 cm can be achieved even at very low slump
values of less than 10 cm – the concrete is thus so
15 stiff that the cone barely collapses under its own
weight. On addition of conventional fluidizers, a
concrete cone having such a low slump would
disintegrate to produce an irregular noncohesive heap
on the spread table after knocking. A spread value can
20 then no longer be reported under these circumstances.
This flow under the action of shear forces is referred
to as plastic viscosity or shear thinning.

The polymers according to the invention thus result in
25 a significantly stronger shear-thinning behavior of the
concrete than conventional fluidizers. This behavior
improves, for example, the pumpability of the
concretes. The shear thinning results not only in a
decrease in energy consumption but also results in
30 suppression of settling of aggregates, which can lead
to blocking of the pump. In addition, such a low
plastic viscosity results in a decrease in the force
which is necessary to pull the pump pipe through the
concrete. In addition, the concrete is less sticky,
35 which has a very positive effect on the processability,
especially in the case of cement-rich concretes. As
mentioned above, the term "rheosmooth" has been
introduced to describe this particular process

property. It is of particularly great importance when particularly cement-rich concretes are employed, as is the case, for example, in Japan. It has hitherto been very difficult to produce this effect by use of
5   conventional fluidizers.

Apart from shear-thinning properties, the polymers of the invention are also able, at an appropriate monomer composition, to reduce the water requirement of the
10   concrete drastically. As Examples C.8 and C.11 show, the water reduction capability of Glenium® 51 can be matched and even slightly exceeded. Although the processability of the concretes produced using the polymers of the invention tends to drop somewhat more
15   over a period of 90 minutes than is the case for Glenium® 27, the spread of Glenium® 27 is in many cases still achieved after 90 minutes despite a lower W/C value, as can be seen from Examples C.3, C5 and C.18.